

Mineral Resources
Consultative Committee

Mineral Dossier No 1

Fluorspar

Compiled by
A J G Notholt BSc, AMIMM, FGS and D E Highley BSc
Mineral Resources Division
Institute of Geological Sciences

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Foreword

I welcome the publication of this dossier.

It is the first of a series which brings together the most recent information about the occurrence, use, and production of the principal minerals of economic importance.

I am sure the dossiers will be a valuable factual basis for the further study of the United Kingdom's mineral resources.

A handwritten signature in black ink, appearing to read 'John Eden', with a long horizontal line extending from the end of the signature.

John Eden
Minister for Industry

Preface

Widespread and increasing interest in the mineral resources of the United Kingdom has led the Mineral Resources Consultative Committee to undertake the collation of the factual information at present available about minerals (other than fossil fuels) which are now being worked or which might be worked in this country. The Committee has produced a series of dossiers, each of which was circulated in draft to the relevant sectors of the minerals industry. They bring together in a convenient form, in respect of each of the minerals, data which had previously been scattered and not always readily available.

It has now been decided to publish these dossiers for general information. This is the first in the series.

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Summary

Fluorspar is an important industrial mineral valued for its calcium fluoride (CaF_2) content, and is the only major source of fluorine. It is used chiefly in the manufacture of hydrofluoric acid and other fluorine chemicals, as a flux in steel making and as an opacifier and flux in the ceramics industry. It has been produced in the United Kingdom for nearly 100 years, the principal deposits occurring in the Pennines of northern England, particularly in Derbyshire and Durham. The deposits are associated with extensive lead-zinc mineralization in the Carboniferous Limestone, the fluorspar at one time being rejected as waste during the working of the lead-zinc mines. This waste material has been worked for many years as a source of fluorspar, although most of the present production is derived from deposits mined underground or at the surface. The fluorspar is usually processed by gravity concentration or flotation. Derbyshire is the principal producing county, much of the present production coming from workings within the Peak District National Park; mining is carefully controlled by the Peak Park Planning Board and restoration conditions are attached to most surface workings.

Reserves in the United Kingdom are considered to be adequate for the next decade, at least, most of the known reserves being in Derbyshire. Additional reserves are likely to be found, particularly in northern Derbyshire and west Durham, beneath geologically younger formations and also at deeper, as yet unexplored, levels of known deposits or mineralised structures. Prospecting and development work has been carried out in a number of areas.

The United Kingdom ranks eighth among fluorspar-producing countries in the world, production in 1969 being about 190,000 tonnes, of which about 106,000 tonnes was of acid grade and 77,000 tonnes of metallurgical grade. Exports in 1969 amounted to nearly 43,000 tonnes valued at about £740,000. There are three major producing companies, Laporte Industries Limited with mines in Derbyshire, Weardale Lead Company, (a subsidiary of Imperial Chemical Industries Limited), and the British Steel Corporation, both of which have mines in Durham. Laporte Industries is the largest producer and is also the only major exporter at present. All three companies consume most of their own production in fluorine chemical manufacture or in steelmaking. There are a number of other producers, many of which sell their output to the larger companies for processing. C E Giuliani (Derbyshire) Limited, an associate of a major Italian producer of fluorspar, plans to produce and process the mineral in Derbyshire.

Definition and mode of occurrence

The term “fluorspar” is usually restricted to the naturally occurring mineral substance consisting essentially of fluorite (calcium fluoride, CaF_2) together with variable amounts of other associated minerals. The theoretical chemical composition of fluorite is 51.3 per cent calcium, 48.7 per cent fluorine, but in nature small amounts of silicon, aluminium and magnesium may also be present due to impurities or inclusions. Yttrium and cerium in trace amounts may substitute for calcium in the crystal structure. Most fluorite, however, contains at least 99 per cent CaF_2 . Fluorite is relatively soft (4 on Mohs' scale), has a specific gravity of 3.18 and may vary in colour from white through yellow, green, violet, blue and brown to black. Its common crystallographic form is the cube, but in most commercial deposits the mineral is massive. *Blue John* or *Derbyshire Spar* is a massive crystalline variety showing curved bands of blue, violet, yellow and purple which has been used for ornamental purposes since the latter half of the 18th century.

Fluorspar deposits occur either as relatively narrow, steeply dipping and vertical veins or lodes, or as flat-lying, irregular masses which may be of considerable size, formed by the replacement of the country rock. The minerals calcite, siderite, ankerite, galena, sphalerite, baryte, quartz and pyrite are commonly also present in these deposits, baryte (barium sulphate, BaSO_4) and galena (lead sulphide, PbS) occurring in sufficient amounts to be commercially recoverable. Sphalerite (zinc sulphide, ZnS) has also been recovered in the past. Fluorite is found also as an accessory mineral in granites and other igneous rocks of similar composition, in veins closely associated with these intrusive masses, and, rarely, as a cementing material in sandstones, but no such occurrences of economic interest are known in the United Kingdom.

Resources

Fluorspar deposits occur chiefly in the Pennines of northern England in limestones of Lower Carboniferous age, within a remarkably mineralised area which witnessed the development of an important lead and iron mining and smelting industry during the 18th century and has also been the source of a substantial production of witherite and barytes, as well as fluorspar. The age of the mineralisation is variable, but most of the workable fluorspar deposits appear to be of late Carboniferous or early Permian age. Outside the Pennines the only occurrences of fluorspar which have been worked have been found in the mineralised region of South-West England, where fluorite is a fairly common mineral constituent of some of the lead and copper lodes.

The Southern Pennines (Derbyshire) area, which includes the important mines near Eyam, accounts for most of the fluorspar produced in the United Kingdom. The deposits form either steeply dipping and vertical fissure veins trending mainly east-west or ENE-WSW, or replacement deposits known as "flats" or "pipes". Some of the veins or "rakes" are 15 m¹ or more in width. The replacement deposits may be of considerable size, one of them, at Masson Hill near Matlock, being at least 500 m long along the strike, up to 250 m wide and up to 15 m in thickness. The most important occurrences are confined to an area extending from Castleton in the north along the eastern side of the North Derbyshire Carboniferous Limestone massif through Bakewell and Matlock, as far south as Wirksworth (*see* Fig 1). Farther to the east deposits are worked also in an inlier of limestone at Ashover and small quantities of fluorspar were formerly produced from the Crich inlier east of Wirksworth. Westwards the veins pass into a zone dominated by baryte or calcite. The veins developed near Eyam often persist for lengths of several kilometres and occasionally attain widths of up to 25 m. In general, however, widths do not exceed 10 to 12 m. To the north of Eyam the vein which forms part of the Hucklow Edge vein system and is worked at the Ladywash mine has an average width of only 2.5 m, while to the south of Eyam a vein averaging 6 m in width was being worked in 1970 at the Sallet Hole mine developed to exploit deposits underlying Longstone Edge.¹

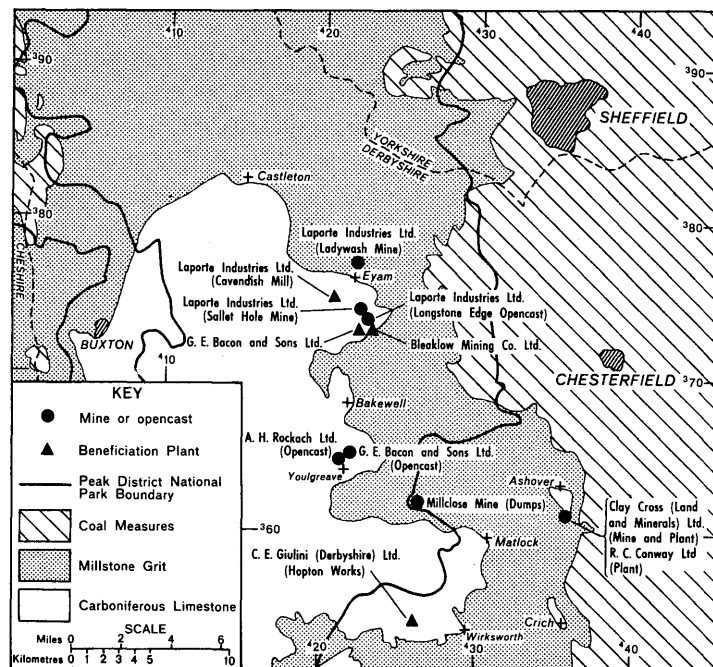


FIGURE 1. LOCATION OF THE MAJOR FLUORSPAR WORKINGS AND BENEFICIATION PLANTS IN THE SOUTHERN PENNINE OREFIELD

1 Metric units are employed throughout this document except where otherwise stated. In most cases this has necessitated the conversion of originally non-metric data. The units and conversion factors used are as follows:

millimetres (mm)	=	inches x 25.4
metres (m)	=	feet x 0.3048
kilometres (km)	=	miles x 1.609344
hectares	=	acres x 0.404686
grammes (g)	=	troy ounces x 31.1035
kilogrammes (kg)	=	pounds x 0.45359237
tonnes (1000 kg)	=	long tons x 1.01605

A considerable proportion of the output in the United Kingdom has been obtained by re-working the waste dumps of old lead-zinc mines in Derbyshire. These dumps carry substantial amounts of fluorspar and were the principal source of supply at the turn of the century, when the basic open hearth method of steel manufacture was introduced. They are still being worked by individuals and small companies with no ore dressing facilities of their own, known as “tributers”, who sell their output to the larger companies for processing.

Important vein and replacement deposits occur also in the Northern Pennine orefield, which extends from the Tyne Valley in Northumberland southwards through parts of Durham, Cumberland and Westmorland to the Craven district of west Yorkshire. Such deposits are worked in west Durham (*see* Fig 2) and west Yorkshire. Mine dumps are not as extensive as in Derbyshire but have nevertheless been re-worked to a considerable extent. Dumps are being worked in Cumberland and on a very limited scale on Grassington Moor and Greenhow Hill in Yorkshire. Additional potential reserves occur in east Cumberland and south Northumberland. Most deposits are found in the thin alternating limestones, sandstones and shales of the Yoredale facies and occasionally in intrusive quartz-dolerite (the Whin Sill), the fissure vein deposits trending ENE, NNW and WNW. Vein widths of up to 9 m have been recorded. As in Derbyshire, mineralisation in the Northern Pennine orefield is zonal, the inner part of the central zone containing the large fluorspar deposits, including those worked in west Durham near Hunstanworth, Rookhope and St John’s Chapel. In the central zone about 14 mines have been active in providing the bulk of the fluorspar output from the Red Vein, near Rookhope in County Durham, which runs ESE–WNW over a distance of some 10 to 11 km and consists of a series of pockets or lenses of fluorite-bearing ore. The vein is up to about 10 m wide. In the Rookhope borehole, which was drilled in 1960–61 near the crossing of the Boltsburn lead vein and the Red fluorite vein, fluorite occurs in the extensively replaced Jew Limestone at depths of between 210 and 215 m, together with sphalerite and some galena. Analyses of the limestone indicate a CaF_2 content of up to 32 per cent. Fluorite occurs also at much greater depths in limestone and in the underlying granite. The Blackdene mine near St John’s Chapel has been developed on one of a series of shorter ENE–WSW veins which intersect the WNW–ESE veins at intervals.

In west Yorkshire, along the southern margin of the Northern Pennine orefield, fluorspar deposits occurring in massive limestone have been worked in the Greenhow Hill and Grassington Moor districts, west of Pateley Bridge. At present some fluorspar is mined and some obtained from dumps on Greenhow Hill, but the small production from Grassington Moor is obtained entirely from old dumps. Fluorspar veins also occur in Wharfedale, Wensleydale and Swaledale. Many of the mineralised veins in east Cumberland and south Northumberland also carry fluorspar. Among these are the deposits formerly worked essentially for lead and zinc in east Cumberland in the Nenthead district and on Rotherhope Fell, south of Alston, where dumps are at present worked for fluorspar, and also in south Northumberland at Coalcleugh near Nenthead and around Allenheads.

In Cornwall fluorspar is widely distributed as a gangue mineral, being frequently associated with copper and lead lodes in slates ("killas") which are mainly of Devonian age, and with tin lodes at depth in granite. Most of the mines which produced fluorspar in the past lie north-west of Plymouth in the Tamar Valley east of Callington. The lodes carry chiefly sphalerite and galena, with fluorite, quartz, baryte and calcite as the gangue minerals and trend roughly north-south. Fluorspar was also produced from the geologically older east-west copper lodes in the Camborne district and near St Day.

Fluorite is a major gangue material in the Liskeard district near Menheniot, particularly in the Wheal Mary Ann, Wheal Hony, Wheal Wray and Wheal Ludcott mines. There is no record that fluorspar has ever been produced commercially from the mines in this area.

Other occurrences

Fluorspar occurs in other parts of the United Kingdom, but generally in minor amounts only. None of the occurrences is considered to be of economic interest at present. In *England* some fluorspar is known to be present in the West Cumberland haematite deposits but has never been worked. Ribs of fluorspar up to 30 cm in width have been recorded from the Brandlehow vein on Catbells on the south-west shore of Derwentwater in the Lake District. Small veins and replacements of fluorspar occur in the Magnesian Limestone of East Durham and the East Midlands. Fluorspar also occurs in the Carboniferous Limestone of the Mendip Hills, Somerset, in the lead orefield.

In *Wales*, fluorite occurs chiefly within the central portions of the Carboniferous lead-zinc orefield of Flintshire and East Denbighshire. For example, fluorspar was the principal gangue mineral at the East Halkyn and Bryn Gwiog mines, but has never been worked commercially at any of the known localities. At the western end of the Great Halkyn lode the fine-grained intermixture of fluorspar and sphalerite gave rise to considerable difficulties in mineral dressing so that substantial quantities of low-grade zinc ore had to be abandoned. The Bryn Gwiog lode yielded a sphalerite concentrate containing as much as 10 per cent fluorspar. South of the East Halkyn mine fluorspar occurs in a few of the lead-bearing veins found between Gwern y Mynydd and the Maeshafn area and, particularly, at the eastern end of the Pant-du vein.

Fluorite is fairly widespread in *Scotland* as an accessory mineral in granite and other igneous rocks and, most frequently, as vein deposits or as a gangue mineral in metalliferous veins. Significant amounts of fluorspar probably occur in a vein containing argentiferous galena and sphalerite worked during the latter half of the 19th century near Ballater in Aberdeenshire. In the Glen Ousdale district of southern Caithness, the mineral forms a stockwork of veinlets in Old Red Sandstone flagstones, and occurs as veins and small pockets in the Helmsdale Granite. Fluorite occurs also in some of the metalliferous veins associated with the Strontian granite in Argyllshire and is widely developed in the Strath area of Skye in the magnetite iron ore and skarn rocks formed by the alteration of the Cambrian Durness Limestone by Tertiary granite. In Morayshire the mineral is very irregularly distributed within the Permo-Triassic Elgin sandstones and is not economically recoverable; locally, however, fluorspar makes up 30 per cent of the entire rock.

No significant occurrences of fluorspar have been recorded in *Northern Ireland*; fluorite has been noted in the Tertiary granites of the Mourne Mountains situated in the southern part of County Down.

Resources of fluorspar in England and Wales were first investigated by the Geological Survey during the First World War as part of a programme to examine mineral deposits. The results were published in 1915 as a Geological Survey memoir (Special Reports on the Mineral Resources of Great Britain, Volume 4). Because of the urgent needs of the domestic steel and chemical industries during the Second World War, a complete re-investigation was carried out by the Geological Survey in collaboration with the Ministry of Supply's Non-ferrous Minerals Development Control. A summary of this survey, which was completed in 1942, was given in a report on United Kingdom mineral resources published in 1949 on behalf of the Westwood (Mineral Development) Committee of the (then) Ministry of Fuel and Power. The details formed the basis of the Fourth Edition of the Geological Survey memoir on fluorspar published in 1952, the most recent authoritative work on the fluorspar resources of the United Kingdom.

Reserves

Known reserves of fluorspar in northern England appear to be adequate for the next decade, but in view of the anticipated increase in demand, a thorough assessment of resources of the known zones of fluorine mineralisation in the Pennine orefields may be desirable. Total known reserves of fluorspar in Durham, Yorkshire and Derbyshire were estimated in 1949 to be about 1.4 million tonnes CaF_2 ; a more recent estimate of reserves in the Southern Pennine and Northern Pennine orefields is tabulated below. According to information received from Laporte Industries Limited, the Glebe operations in the Southern Pennine orefield are based on large reserves of ore. The aim of the company is always to maintain not less than 15 years' proved reserves.

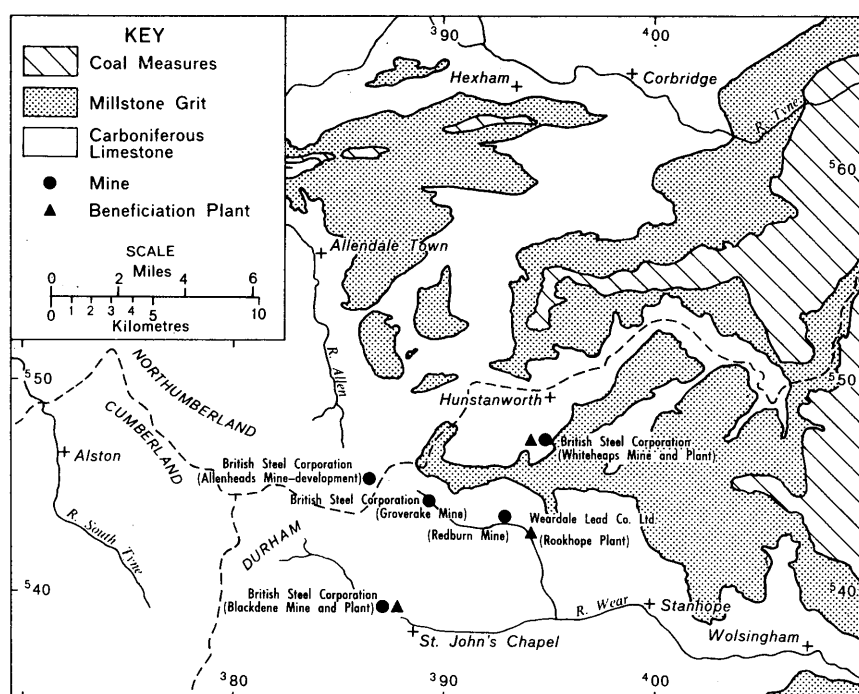


FIGURE 2. LOCATION OF THE MAJOR FLUORSPAR WORKINGS AND BENEFICIATION PLANTS IN THE NORTHERN PENNINE OREFIELD

Fluorspar reserves in the Southern Pennine and Northern Pennine orefields

Location	Average CaF ₂ content	Proved and probable reserves		Prospective reserves		Total reserves	
		Quantity	CaF ₂ content	Quantity	CaF ₂ content	Quantity	CaF ₂ content
	<i>Per cent</i>	<i>million tonnes</i>		<i>million tonnes</i>		<i>million tonnes</i>	
Southern Pennine orefield	35	4	1.4	16	5.6	20	7.0
Northern Pennine orefield	60	1	0.6	4	2.4	5	3.0
Total	—	5	2.0	20	8.0	25	10.0

Source: Industrial Minerals, 1970, No. 31, p. 26.

Most of the more easily accessible deposits have probably already been discovered and worked, so that new occurrences will be more difficult and expensive to find and assess. Further workable deposits may well be found, particularly in northern Derbyshire and west Durham. Workable reserves are likely to be discovered also in east Cumberland and south Northumberland.

In the Northern Pennine orefield new deposits may be found where favourable horizons, such as the Main or Great Limestone, or sandstones thickened in delta channels, lie concealed beneath younger formations, and at deeper or unexplored levels of known deposits or mineralised structures.

Furthermore it might be possible to extract a significant tonnage of fluorspar from material back-filled into extensive old stopes, or from bodies rich in fluorspar, more or less free from galena, which were left in place or were not investigated during former lead mining operations.

Similar considerations apply to the Southern Pennine (Derbyshire) orefield where there is a strong likelihood of deposits being found at depth beneath the present shallow workings or on sections of unworked veins. Near Eyam, for example, exploratory work revealed an unworked section of the Old Edge vein which contained about 60 per cent CaF₂ and 2 per cent PbS. Unlike the Northern Pennine orefield there is a strong development of fluorspar-rich 'flats' which are difficult to locate except when present at the surface.

As in the Northern Pennine orefield important reserves of fluorspar may occur also beneath the cover of younger rocks to the east of the main Carboniferous Limestone outcrop. There are indications that fluorine

mineralisation extends to the depths greater than those at present reached by mining. For example, fluorspar, baryte and calcite have been recorded in an oil boring at Eakring in Carboniferous Limestone at depths exceeding 760 m below the surface.

Furthermore, it might be possible to extract a significant tonnage of fluorspar from waste which was previously back-filled into the stopes of old lead and zinc mines or from mine dumps and tailings associated with these mines. There is also a possibility that bodies rich in fluorspar, but more or less free from galena, may still remain underground in abandoned lead mines where they were left in place or not fully investigated when the mines were active. Tailings associated with the Millclose mine in Derbyshire, one of the world's most productive lead mines before the Second World War, are reputed to amount to at least 750,000 tonnes of material containing 22 to 25 per cent CaF_2 and 4 per cent lead and zinc.

There has recently been a marked increase in exploratory activity in the Pennine orefields companies involved including Mineraria Silius SpA (a subsidiary of the Italian C. E. Giuliani group) and Alcan Aluminium Limited in Derbyshire and Anglo Swiss Aluminium Company Limited (a subsidiary of Alusuisse) in Co Durham. Extensive fluorine mineralisation has been discovered in Derbyshire near Bonsall, south-west of Matlock, near the Ball Eye limestone quarry owned by Pitchmastic Quarries Limited, a subsidiary of the FPA Construction Group Limited. A number of deposits have been opened up near the quarry which supply ore to Giuliani's Hopton works. In west Durham the British Steel Corporation (United Steel Companies Limited) have begun an extensive prospecting programme near Allenheads, north-west of St John's Chapel.

Land use

With the possible exception of small operations based on old mine dumps, all fluorspar workings are subject to permissions under the Town and Country Planning Acts, which for surface workings will include restoration conditions. In some cases, where an old tip retains its original appearance as a heap of waste material deposited on the ground, it will be treated as a 'chattel' (ie moveable possession) and hence planning permission for working it will not be required. Removal of such heaps should, however, tend to decrease rather than increase dereliction.

All the current workings are within the uplands of the Pennines, which in Durham and west Yorkshire are in areas of rough grassland and moorland but in Derbyshire involve some areas of reasonable quality pastureland. Estimates of land covered by current permissions for fluorspar workings, both surface and underground are:

Durham and Cumberland	—	65,000 acres [26,300 hectares] of which over 54,000 acres [21,900 hectares] is the Stanhope Common permission of Weardale Lead Company (ICI Limited)
West Yorkshire	—	about 250 acres [100 hectares]
Derbyshire	—	7,000 acres [2,800 hectares] (probably not including some smaller workings).

Some reserve areas amounting to about 4,000 acres [1,600 hectares] have been defined in the Development Plan for Durham, in which other land uses will not be allowed to sterilise future fluorspar interests.

Fluorspar was itself largely a waste product from metalliferous mining until about 1890, so that a considerable part of present production comes from the re-working of old mine dumps or back-filling in underground veins. Some of the associated vein minerals are now separated at the larger treatment plants and sold.

A considerable proportion of the existing permissions is for underground working, which does not normally affect the surface of the land. Modern underground workings are not likely to give rise to subsidence. Older, shallow workings in some of the mineralised veins (originally worked as metalliferous ores with the fluorspar discarded as waste) have given rise to narrow zones of subsidence, and could still do so in the future. These unstable old workings can complicate present mining, although their general distribution is known and can be clearly seen on aerial photographs. Possible further subsidence from such workings could be controlled only where they coincide with areas of opencast working down to the level of the bottom of the previous extraction.

Population densities in the North Pennines and Yorkshire areas of extraction are very low, but are somewhat higher in Derbyshire. The effect on built-up areas is therefore small. Agriculturally the value of the land is usually negligible.

The most controversial aspect is the effect of workings on amenity, particularly in Derbyshire, since with the exception of the Bonsall and Ashover extraction areas the output comes entirely from within the Peak District National Park. The Peak Park Planning Board recognise the importance of the mineral and in their Report of Survey published in 1966 state (page 19) that "the scarcity and the specific location of the deposits will necessitate continued extraction within the National Park". The Board have, however, opposed the opening of some unworked mineral veins in areas of special scenic importance. In some cases the re-working of grassed-over dumps for fluorspar has been detrimental to the landscape, while in other cases levelling of dumps by such workings with subsequent restoration can lead to an improvement in the agricultural quality of the land. There have been objections to developments near Eyam because of conspicuous heaps of spoil and areas of tailings dams, and also to possible development of deep, opencast workings along some of the "rakes" such as those on Longstone Edge. The Grassington Moor area of the West Riding is within the Yorkshire Dales National Park. The Greenhow Hill workings fall just outside this Park, although they are within an "area of great landscape value", as is the Northern Pennine orefield.

The Derbyshire mines are governed by the traditional Barmote Courts which were invested with statutory powers by Act of Parliament in 1852.

Uses

The principal uses of fluorspar are in the manufacture of fluorine chemicals, chiefly hydrofluoric acid; as a flux in metallurgical operations, chiefly in steel manufacture; and to a lesser extent, as an opacifier and flux in the ceramic industry. Fluorspar is used also in making mineral wool, glass fibre, pottery and ceramic jewellery, in brick making to prevent staining and as a bonding material in abrasive wheels. High-grade fluorspar is used in the manufacture of special optical lenses, particularly those for use in microscopes. Blue John or Derbyshire Spar is used in the manufacture of vases, ashtrays and other decorative objects.

Hydrofluoric acid (HF) is produced by the reaction of acid-grade fluorspar (normally containing a minimum of 97 per cent CaF_2) with sulphuric acid in heated kilns or retorts. About 2.2 tonnes of acid-grade fluorspar are required to produce one tonne of hydrofluoric acid. Calcium sulphate is formed as a waste product. Lower grades of fluorspar are unsatisfactory because of the formation of fluosilicic acid from quartz or because of frothing resulting from the presence of carbonates. Fluorspar is an essential raw material for the manufacture of aluminium fluoride (AlF_3) and artificial cryolite (Na_3AlF_6),

which are used as fluxes and electrolytes in the production of primary aluminium. Production of one tonne of aluminium requires cryolite and aluminium fluoride equivalent to 58 to 60 kg of acid-grade fluorspar. Another important use is in the manufacture of fluorocarbons, via hydrofluoric acid, for the preparation of aerosols, plastic, refrigerants, blowing agents for urethane foams, polymers and fire extinguishing gases. The acid is used also as a catalyst in petroleum alkylation, in steel pickling, enamel stripping, and in various electroplating operations. The production of uranium tetrafluoride (UF_4) is an intermediate stage in the production of uranium metal and in the preparation of uranium hexafluoride (UF_6), which is used in the separation of uranium isotopes. Fluorides are used as insecticides and preservatives, antiseptics, ceramic additions, and in electroplating solutions.

Fluorspar is used as a flux in the production of steel by the basic open hearth, electric arc and basic oxygen (BOF) processes, and also in the electro-slag refining process for making high grade steel and certain alloys. The mineral gives fluidity to the slag, resulting in a better steel recovery and lower fuel cost. It also enables the maximum amount of lime to be made available for effective removal of sulphur and phosphorus from the steel to the slag. Approximately 1.3 to 3.1 kg of metallurgical-grade fluorspar are consumed per tonne of crude steel produced by the open hearth process, 3.6 to 4.5 kg in electric furnaces, and 5.4 to 7.1 kg by the basic oxygen process. The gradual replacement of the open hearth process by the basic oxygen method of steel production is having an important effect on the demand for metallurgical-grade fluorspar. In the electro-slag refining process for making high-grade steel and certain alloys, acid-grade fluorspar is required rather than the lower-grade material used in the other methods of steel production. The process is one which has been developed by the British Iron and Steel Research Association since 1962 and has become commercially important during the last four years. Fluorspar may also be used in the production of ferro-alloys, iron castings, as a flux in magnesium reduction, and in zinc smelting by the horizontal retort process.

In the ceramic industry fluorspar is added in very variable amounts to glass melts, enamels and glazes as a flux and opacifier. Opal glass demands larger quantities of fluorspar than does clear glass. For optical purposes, colourless or nearly colourless crystals of fluorite free from flaws are used and should be of sufficient size to enable plates of $\frac{1}{2}$ in [13 mm] to 2 in [51 mm] in diameter to be cut.

Specifications

There are three principal market grades, the specifications for which are fairly well defined, although the requirements of individual consumers often vary considerably in detail.

Acid-grade fluorspar is required to be as fine grained as possible and consumers call for material substantially less than 100 British Standard mesh in size. Flotation concentrates are therefore very suitable but even so some consumers undertake their own fine grinding. Very strict chemical specifications are also imposed; normally the concentrate must contain a minimum of 97 per cent CaF_2 , with a maximum of 1 per cent SiO_2 and 1 per cent CaCO_3 and very low sulphur (0.03–0.05 per cent) and metal contents. A lower CaF_2 content may be acceptable in some cases if the SiO_2 content is proportionately lower.

Size specifications for *metallurgical-grade* fluorspar range from 4 in [102 mm] to 1/8 in [3 mm] fluorspar ('lump' and 'gravel' spar) with only a small percentage of 'fines' (less than 1/8 in [3 mm]). Specifications indicate a minimum CaF_2 content ranging from 70 to 85 per cent, in certain exceptional instances a maximum of up to 12 per cent SiO_2 , and only trace amounts of sulphur and metals. Much of the output of this grade appears to be sold on the basis of a minimum of about 80 to 85 per cent CaF_2 and a maximum of 6 per cent SiO_2 . Silica (SiO_2) is an objectionable impurity in the steelmaking process, chiefly because it neutralises some of the CaF_2 present. For this reason, most metallurgical-grade fluorspar is sold in terms of "effective units" of CaF_2 usually expressed as "effective per cent of CaF_2 ". This figure is normally obtained by subtracting 2½ times the percentage of SiO_2 from the percentage of CaF_2 in the fluorspar concentrate. However, there is some evidence that this method of calculation is open to question. In foundry practice, at least, the presence of silica is perhaps not quite so critical as is alleged. The presence of barytes is also undesirable because it reduces the fluidity of the slag.

Ceramic-grade fluorspar must be fine grained (eg more than 75 per cent between 16 and 150 mesh and less than 25 per cent minus 150 mesh) and should contain a minimum of 93 to 95 per cent CaF_2 , with a maximum of 3 per cent SiO_2 , 0.12 per cent Fe_2O_3 , and 1 per cent CaCO_3 . For brown glass the Fe_2O_3 content may be considerably higher. Only traces of lead, zinc, barium and sulphur are normally permitted.

Specifications for fluorspar are not included in British Standard or other authoritative publications, but there are British Standard specifications for wood preservatives consisting essentially of fluoride-arsenate-chromate-dinitrophenol mixtures (BS 3453:1961); the analysis of fluoride opal glasses (BS 2649: Part 4:1963), and the chemical composition and methods of testing for fluoroboric and metallic fluoroborates (BS 2657:1956) used for electroplating.

Price and cost

Nominal prices for fluorspar are published regularly in the journal *Industrial Minerals*. Quotations for October 1970 are as shown below:

Metallurgical grade, min 70 per cent CaF_2 , ex UK mine: £9 to £13 per long ton [£8.86 to £12.79 per tonne].

Acid grade, dry basis, 97 per cent CaF_2 , bagged del UK: £19 to £22 per long ton [£18.70 to £21.65 per tonne].

Ceramic grade, ground, 93–95 per cent CaF_2 , CIF: £12 to £15.10s. per long ton (£11.81 to £15.26 per tonne).

The quotations published for November 1970 show an increase in the price of acid-grade fluorspar to £20 to £24 per long ton (£19.68 to £23.62 per tonne) and of ceramic-grade fluorspar to £16 to £19 per long ton (£15.75–£18.70 per tonne). Similarly the price of metallurgical-grade fluorspar has been raised since March 1971 to £11–£15 per long ton (£10.82–£14.77 per tonne). These prices relate to fluorspar shipped in bulk. Most of the trade in fluorspar is subject to long term (five year) contracts.

The cost of processed fluorspar is small in relation to the cost of such products as steel, aluminium and fluorocarbons, in the manufacture of which fluorspar is used. The transport element has always represented a high and increasing proportion of total price to the consumer except in those cases where delivery distance is negligible. It could be as much as 30 per cent of the delivered price of metallurgical-grade fluorspar. Fluorspar deposits being worked occur chiefly in the north Derbyshire and west Durham areas, so that transport costs to the Scottish and South Wales steelworks, for example, will be considerably higher than those borne by steelworks in Sheffield.

The modern tendency is to handle dried flotation (acid-grade) concentrates in bulk. The cost of bagging is thereby eliminated and handling is greatly facilitated. Similar considerations apply to metallurgical and ceramic grades of fluorspar. Some of the fluorspar filter cake produced by Laporte Industries Limited bypasses the dryers and is shipped in bulk to North America. Wet filter cake contains up to 10 per cent moisture.

Technology

Working and processing

Fluorspar deposits are worked by both underground and opencast mining methods, the ore produced by the major companies in the United Kingdom generally containing 40 to 50 per cent CaF_2 , with a cut-off grade of 30 per cent. At one of the mines developed by Laporte Industries Limited in Derbyshire the vein rock generally averages about 55 to 65 per cent CaF_2 . In addition fluorspar is produced by tributaries from mine dumps, which they own or lease; some tributaries carry out small underground and opencast operations to obtain fluorspar back-filled into old workings. Open sub-level stoping is employed at the Ladywash mine north of Eyam in northern Derbyshire, where the shaft is 220 m deep. Caving is being employed at the neighbouring Sallet Hole mine, with an adit 360m in length providing access to the vein system underlying Longstone Edge. Fluorspar veins outcropping on Longstone Edge near Eyam are worked by opencast methods using tractor-mounted rippers and a dragline to excavate the ore. Shafts have been developed to depths of 180 m in Durham.

Mined fluorspar is delivered to a stockpile and often blended before use so as to maintain a fairly constant feed for the beneficiation plant. From the stockpile the ore is generally crushed, washed and screened before further processing, essentially to meet market specifications in terms of CaF_2 content. Very high grade fluorspar deposits have been treated in the past mainly by crushing, screening and hand-sorting methods, but with the use of lower-grade

ores, additional and more sophisticated beneficiation techniques have become necessary. The type of beneficiation plant erected depends upon the grain size, the mode of occurrence of fluorspar and the quality of the product desired, as well as upon the nature of the gangue minerals. At some plants fluorspar for use in steel manufacture is produced by washing and jigging only.

Most modern beneficiation plants use a combination of gravity and flotation processes. Gravity concentration is usually a delicately controlled operation, chiefly because the density differential between fluorspar and most of the usual gangue minerals is small, the specific gravities being: fluorspar 3.18, calcite 2.72, quartz 2.65. (The specific gravities of baryte and galena are 4.5 and 7.5 respectively.) Jigs, formerly much favoured, have been largely replaced by heavy-medium separation (HMS) units, typically employing a high-density medium consisting of ferrosilicon in water which has a specific gravity of 2.8. The purpose of a heavy-medium separation plant is usually to produce a coarse, metallurgical-grade fluorspar and to provide a preconcentrate which is then used as a feed for the flotation plant. Old lead-zinc tailings and dumps, which assay up to 40 per cent fluorspar, can be treated to provide a product analysing 85 to 90 per cent CaF_2 .

The presence of silica in workable fluorspar deposits containing more than 30 per cent CaF_2 frequently poses considerable problems. For example in the Derbyshire orefield silicification of the wall-rocks with microcrystalline quartz or chalcedony is very widespread, while the fluorspar itself tends to contain small siliceous inclusions. In extreme cases liberation and removal of the silica can be effected only by very fine grinding. As a result the product cannot meet specifications for metallurgical-grade fluorspar in terms of particle size distribution. However, by the use of briquetting or pelletising techniques material acceptable to the metallurgical industry may be provided.

Flotation of fluorspar is a well-established process which is commonly used where a relatively pure product, such as acid-grade fluorspar, of fine particle size is required. In some cases one or more concentrates of lower grade may be produced which are sold as ceramic-grade or are briquetted or pelletised and sold as metallurgical-grade fluorspar. Foundry fluxes based upon, or largely comprising fluorspar, are prepared in briquetted or pelletised form to facilitate measurement and use, and also to eliminate wastage. This trend is developing also for the heavy steel industry in the USA and is likely to become a feature of the United Kingdom steel industry. Individual plants vary considerably in complexity depending on the condition of the ore.

The accompanying flow sheet (Fig 3) shows the beneficiation of fluorspar at the Cavendish mill operated by Laporte Industries Limited near Eyam in Derbyshire, which is one of the largest and most efficient in Europe. The +3/8 in -2 in [+10 mm-51 mm] solids provide a feed for heavy media separation, which is carried out first at a specific gravity of 2.80, when silica and limestone float are removed as tailings, all the heavier minerals sinking. A second separation at a specific gravity of 3.25 removes metallurgical-grade fluorspar in the float. The limestone-silica tailings and the metallurgical-grade

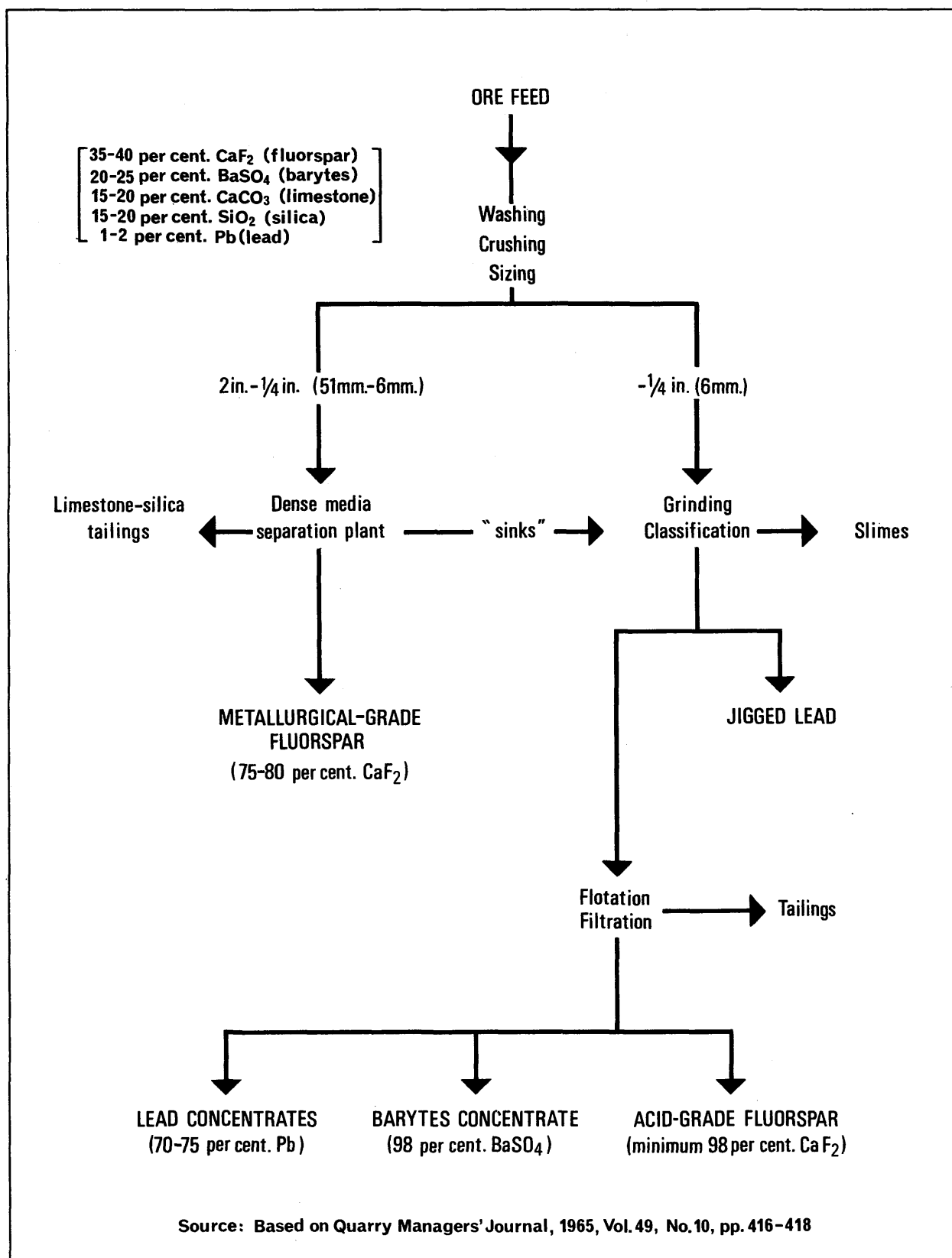


FIGURE 3. SIMPLIFIED FLOW DIAGRAM OF THE CAVENDISH MILL NEAR EYAM, DERBYSHIRE

fluorspar may be produced to any size below 2 in [51 mm] in separate crushing and screening units and are sold without further treatment; the third fraction (the "middlings") of high galena and barytes values is ground to provide an additional feed for flotation. The flotation feeds are ground and after classification produce a pulp substantially minus 100 mesh, from which galena, fluorspar and barytes, in that order, are recovered. The lead concentrate is sold as filter cake without drying. Most of the fluorspar is dried and stored in silos for despatch by road tanker, or packing in bags. The barytes filter cake is dried and part of the product ground. Both grades are despatched by bulk tanker. The tailings are sold as road metal or as concrete aggregate.

Research

Research is undertaken by the major producing and consuming companies, to enable marketable grades of fluorspar to be produced economically from the lower grades of ore. The introduction of heavy-media separation plant, for example, has made it possible to treat material rejected in the past, such as old tailings, which may contain up to 40 per cent fluorspar.

Traditionally only 'gravel' or 'lump' fluorspar could be used for fluxing purposes, but successes achieved with briquetted and pelletised fluorspar for metallurgical and foundry use have created a market for the fluorspar 'fines' produced during processing. Fluorspar briquettes and pellets are generally superior to natural metallurgical-grade fluorspar or "gravel" spar in having more uniform composition and in being easier to handle. Briquettes are particularly suitable for use in foundries using hot blast cupolas as no fluorspar is lost in the blast and the briquette reaches the melting zone before disintegrating.

Pellets are produced by combining finely ground fluorspar with an organic binder. Fluorspar from the flotation process together with the binder are fed continuously into a shallow, tilted, rotating pan. As the pan rotates the fluorspar mixes with the binder and forms balls or pellets which spill over the top of the pan when they reach the desired size. The balls or pellets are then carried to an oven where the excess water is driven off and the pellets hardened. The size of the pellets can be controlled by varying the angle and tilt of the pan, the speed of rotation and the moisture content.

The Clay Cross Company who specialise in the manufacture of fluorspar briquettes for foundry use produce cylindrical briquettes which are 5¼ in [133 mm] long, 3½ in [89 mm] in diameter and weigh 4¼ lb [1.93 kg]. A coarser grade fluorspar is used than in pelletisation and the briquettes are pressed in moulds, hardening being achieved chemically without the use of ovens.

Production

The United Kingdom is self-sufficient in fluorspar and in 1969 ranked eighth among the major producing countries (*see* Table 1). It is estimated that a total of about 4 million tonnes of fluorspar has been produced in the United Kingdom to the end of 1969. Annual recorded production amounted to about 190,000 tonnes in 1969, compared with 172,000 tonnes in 1968¹.

¹ Production recorded by The British Fluorspar Producers Development and Research Association. These figures do not include the output of some producers who are not members of the Association.

Table 1. World production of fluorspar, 1964–1969, by major producing countries

<i>Producing country</i>	<i>Thousand tonnes</i>					
	1964	1965	1966	1967	1968	1969
Mexico	643	735	726	785	926	1,007
USSR (estimated)	300	350	350	380	380	400
Spain	150	221	223	285	309	365
Thailand	64	52	48	133	245	298
France	195	196	215	244	261	280
Italy	125	153	195	205	225	258
China (estimated)	200	220	250	250	250	250
United Kingdom	109	131	155	154	172	190
USA	197	219	230	268	229	164
South Africa	60	66	82	95	109	150
Canada (estimated)	90	100	70	80	100	110
World total (estimated)	2,400	2,800	2,800	3,200	3,500	3,800

In order to produce a marketable output of this order a considerable quantity of ore has to be mined or processed, as is shown by the following Ministry of Power figures for 1968, which are based on original returns from individual operators:

<i>County</i>	<i>Crude ore mined</i>	<i>Crude ore processed</i>
<i>Tonnes</i>		
Durham and Cumberland	63,738	55,327
Derbyshire	359,611	371,036
West Yorkshire	139	—
Total	423,488	426,363

Recorded production of fluorspar, by grades, for the period 1947–1969 is shown in Table 2, the considerable increase during the mid–1960's being the result chiefly of the expansion of operations by Laporte Industries Limited in northern Derbyshire.

Table 2. United Kingdom: Recorded production of fluorspar, by grades, 1947–1969

<i>Year</i>	<i>Tonnes</i>			
	<i>Metallurgical</i>	<i>Acid</i>	<i>Ungraded</i>	<i>Total</i>
1947	39,754	6,459	18,145	64,358
1948	43,626	9,547	13,372	66,545
1949	48,698	9,504	9,373	67,575
1950	45,598	8,608	9,813	64,019
1951	53,846	10,561	11,547	75,954
1952	50,209	12,315	14,516	77,040
1953	53,024	13,349	14,025	80,398
1954	53,382	17,741	12,889	84,012
1955	54,917	19,007	13,378	87,302
1956	62,683	20,393	9,943	93,019
1957	65,901	22,144	6,726	94,771
1958	50,240	23,739	4,770	78,749
1959	52,977	26,296	5,166	84,439
1960	62,228	34,145	2,735	99,108
1961	49,313	34,807	2,646	86,766
1962	37,314	31,974	3,607	72,895
1963	44,259	39,578	4,660	88,497
1964	55,804	50,320	3,370	109,494
1965	62,946	66,354	1,702	131,002
1966	65,446	82,219	6,989	154,654
1967	59,311	89,471	5,596	154,378
1968	63,982	100,301	7,315	171,598
1969	77,315	106,580	6,402	190,297

Source: The British Fluorspar Producers Development and Research Association.

The relative increases in the production of acid-grade and metallurgical-grade fluorspar during the period 1947–1969 are also shown graphically in Fig 4. The production of acid-grade fluorspar has increased very substantially rising from 17,741 tonnes in 1954 to 106,580 tonnes in 1969. This increase is due to the large expansion of the fluoride chemical industry chiefly in the mid–1960's, and the growth in demand for uranium in nuclear power stations. The production of metallurgical-grade fluorspar, apart from some significant fluctuations, has risen by about 20 per cent in the past 15 years. One important development in steel making has been the perfection and growing use since the early 1960's of the basic oxygen furnace (BOF) process which uses much greater quantities of higher grade fluorspar. The quantities produced for the ceramic industry have not varied greatly.

Some of the vein minerals associated with fluorspar are separated at the larger treatment plants and sold. In 1968, for example, over two-thirds of the total United Kingdom lead ore production of 3,251 tonnes (in terms of contained metal) was obtained as a by-product of fluorspar processing. It is estimated that a substantial proportion of the total barytes output of 24,337 tonnes in 1968 was also derived from this source.

Production of fluorspar for ornamental purposes began in Derbyshire in about 1775 and, according to official records, small quantities were produced from about the 1850's in Cornwall and Devon, probably for use in non-ferrous metallurgy. Northern Derbyshire and west Durham became the main sources in the United Kingdom when substantial fluorspar production began at the turn of the century, following the introduction of the basic open hearth steel-making process. In addition small quantities were produced in west Yorkshire. Fluorspar mining in South-West England was not on a large scale and records are far from complete, recorded production during the 19th century being only about 4,500 tonnes. There has been no production in Scotland, Wales or Northern Ireland.

Production figures, by principal grades of fluorspar, have been made available for many years to the production department (at present the Department of Trade and Industry) by the British Fluorspar Producers Development and Research Association formed in 1944. However, these figures do not include fluorspar produced by non-members of the Association, with the exception of the important output of the British Steel Corporation (United Steel Companies Limited). It is estimated that there is therefore an additional 'outside' production of up to about 10 per cent. United Kingdom fluorspar production statistics based on figures supplied by the Association are published annually in the 'Statistical Summary of the Mineral Industry' prepared by the Mineral Resources Division of the Institute of Geological Sciences. Production statistics published annually by the Department of Trade and Industry in its 'Digest of Energy Statistics' are compiled from returns received from individual producers, although small amounts of fluorspar obtained from old mine dumps, for which no returns are submitted, may be excluded. It seems certain that both crude ore and dressed (concentrated) material are included in the initial compilation. The latest figures from this source are:

	1965	1966	1967	1968	1969
<i>Tonnes</i>	117,000	149,000	148,000	196,000	188,000

The present official series of production statistics, begun by the Mines Department and continued by the Ministry of Power, goes back to 1873. This series covers newly-mined fluorspar and excludes material recovered from old lead and zinc mine dumps. It shows a total production of 4 million tonnes during the 97-year period 1873–1969, of which 3.9 million tonnes has been produced since 1905.

Overseas trade and consumption

The United Kingdom is fortunately not only self-sufficient in fluorspar but is also a substantial exporter. Exports make a useful contribution to the balance of payments and were valued at about £750,000 in 1969. The net benefit has quadrupled between 1964 and 1969 and further increases in export earnings are anticipated.

United Kingdom import and export statistics for fluorspar are not separately recorded. As there is only one major United Kingdom exporter (Laporte Industries Limited) the publication of official export statistics may be withheld for reasons of confidentiality. However, trade statistics are grouped in such a way that it is possible to estimate the quantities and values of both exports and imports of fluorspar.

Exports

Until 1969 fluorspar was included in the official United Kingdom export statistics under the heading: Statistical Code No E276 53: Quartz; quartzite; cryolite and chiolite¹, natural; feldspar, leucite, nepheline and nepheline syenite; fluorspar. Exports under this heading for the period 1964–1969 are given in Table 3 and probably consist wholly or largely of acid-grade fluorspar.

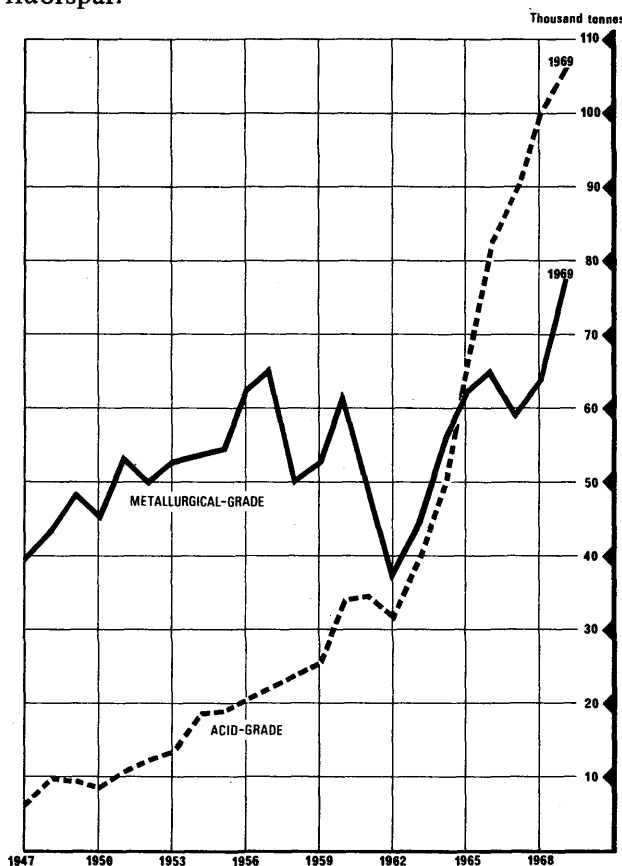


FIGURE 4. U.K. RECORDED PRODUCTION OF ACID-GRADE AND METALLURGICAL-GRADE FLUORSPAR 1947–1969

¹Na₂AlF₆

Table 3. United Kingdom: Estimated exports of fluorspar, 1964–1969

<i>Tonnes</i>						
To:	1964	1965	1966	1967	1968	1969
Japan	1,912	1,001	2,103	3,511	5,565	12,870
Canada	1,315	2,800	3,557	2,966	7,701	10,069
Australia	2,232	3,533	7,129	4,141	8,293	6,291
Netherlands	(a)	(a)	1,593	4,464	6,997	2,628
Irish						
Republic	1,459	2,114	1,459	757	1,119	1,432
India	791	1,095	2,570	1,118	706	1,180
Norway	1,093	1,179	1,305	340	1,213	1,047
Finland	617	752	721	362	537	751
Turkey	555	(a)	(a)	204	327	454
Sweden	(a)	1,821	1,939	928	2,539	316
USA	(a)	4,704	(a)	19,212	14,726	6
Other countries	3,245	2,901	1,949	2,711	5,103	5,889
Total	13,219	21,900	24,325	40,714	54,826	42,933
f.o.b. value	£185,158	£303,125	£370,205	£594,187	£924,286	£740,186

Source: HM Customs and Excise.

(a) Quantities, if any, included with 'Other countries'.

Since January 1970 exports have been recorded under a somewhat narrower heading: Leucite, nepheline and nepheline syenite; fluorspar. In the year ending December 1970, these amounted to 51,000 tonnes, valued at £803,000. Again it is believed that these figures relate almost entirely to acid-grade fluorspar. Probably about 25 per cent of the total United Kingdom output is exported. In 1968 sales were made by Laporte Industries Limited to 23 countries, including the USA, Canada, Australia, Japan and India. As world demand is expected to increase substantially over the next few years, domestic exports can be expected to increase significantly in view of present plans for expansion of domestic milling capacity in Derbyshire.

Imports

Imports are only of very marginal importance. Small tonnages of fluorspar are imported chiefly from China and South Africa, mainly, it is understood, for ceramic use and lens manufacture. These are not separately recorded by HM Customs and Excise, but are included in the heading: Statistical Code No 276 67: Leucite, nepheline and nepheline syenite; fluorspar. The principal imports recorded under this heading are from Norway and Canada and these almost certainly consist of nepheline-syenite. The remainder, however, provide possibly the best indication that is available at present of United Kingdom imports of fluorspar, the figures for 1963–1969 being shown in Table 4.

Table 4. United Kingdom: Estimated imports of fluorspar, 1964–1969

	<i>Tonnes</i>					
From:	1964	1965	1966	1967	1968	1969
China	—	—	501	500	—	—
France	10	—	—	—	—	—
Italy	—	—	—	16	—	—
Mexico	—	—	—	—	1	—
Netherlands	—	—	—	—	101	—
South Africa	—	—	63	114	—	—
Spain	—	—	10	14	—	51
Sweden	200	—	—	—	—	—
USA	186	46	—	—	—	—
Total	396	46	574	644	102	51
c.i.f. value	£5,753	£1,637	£6,091	£9,673	£1,245	£1,151

Source: HM Customs and Excise.

Consumption

There are no published statistics relating to the consumption of fluorspar in the United Kingdom. However, as imports of fluorspar are negligible, an approximate measure of the quantity of fluorspar consumed may be arrived at by deducting estimated exports from production. Precise figures cannot be arrived at because of the incomplete nature of import and export statistics. Apparent total consumption in the United Kingdom in 1969 was probably about 147,000 tonnes, of which 77,000 tonnes was used for metallurgical purposes and about 64,000 tonnes by the chemical industry. Similarly, for the period 1964–1969 the amount of home production retained for use in this country appears to have averaged about 119,000 tonnes per annum i.e. recorded production of about 152,000 tonnes less estimated exports of about 33,000 tonnes.

Demand trends

There has been a steady increase in fluorspar consumption in the United Kingdom in recent years, which reflects the increasing demands of the steel and chemical industries; the amount of fluorspar used in ceramics and for other purposes has remained relatively constant. The anticipated expansion of the steel and chemical industries and of the aluminium industry will lead to further increases in consumption. The United Kingdom fluorspar industry may be regarded as having begun a phase of significant expansion. Assuming that the various projects which have been reported come to fruition, it is estimated that production capacity will exceed 300,000 tonnes per annum, of which at least one-third would represent an exportable surplus.

In general the world demand for both acid-grade and metallurgical-grade fluorspar is likely to increase substantially during the next 10 years. It has been estimated that world requirements for fluorspar could exceed 6 million tonnes by 1975, compared with the world production of 3.8 million tonnes in 1969. Substantial production of fluorspar began at the end of the 19th century, after the introduction of the basic open hearth steel-making process. The fluorspar industry gained further impetus with the increase in steel production during the two world wars. During the 1950's the amount of fluorspar used per tonne of steel was steadily reduced, but this trend is being reversed by the increasing use of the basic oxygen process, which requires greater quantities of fluorspar per tonne of steel produced. In terms of total United Kingdom steel output the open hearth and basic oxygen methods consume approximately equal tonnages of fluorspar at present but with the wider adoption of the basic oxygen process the demand for metallurgical-grade fluorspar will increase considerably. According to the Benson Committee Report published in 1966 United Kingdom crude steel output may reach 35.5 million tons [36.1 million tonnes] by 1975. In 1969 crude steel production amounted to about 26.8 million tonnes, so that an additional 40,000 to 60,000 tonnes of fluorspar might be required by 1975, depending on the speed with which basic oxygen furnaces are introduced.

The quantity of fluorspar used for hydrofluoric acid manufacture has also increased rapidly. Requirements of acid-grade fluorspar (including ceramic-grade material) are reported to be about 55,000 to 60,000 tonnes at present, and are met entirely by domestic production. The largest potential growth is expected to be in the fluorocarbon industry, but other applications such as in metal treatment (steel pickling), are also likely to expand. Organic and inorganic fluorine chemicals are produced chiefly by Imperial Chemical Industries Limited, Imperial Smelting Corporation and Laporte Industries Limited. Another reason for the marked expansion in hydrofluoric acid production is the important role that this acid plays in the manufacture of aluminium fluoride and synthetic cryolite, which are used in the production of aluminium. The annual capacity for primary aluminium production in the United Kingdom, which amounted to about 40,000 tonnes in 1969, is to be raised to about 300,000 tonnes in 1971 by the construction of three plants, for which an additional 15,000 to 16,000 tonnes of acid-grade fluorspar is likely to be required. Annual capacity may reach about 400,000 tonnes of aluminium by about the mid-1970's, for which, perhaps, a further 6,000 tonnes of fluorspar will be needed, assuming that the necessary plant becomes available for converting fluorspar to aluminium fluoride and artificial cryolite. New processes in the aluminium industry and increased reclamation of fluorides from pot linings and cell gases may reduce somewhat the amount of fluorspar required per tonne of aluminium produced, but the saving effected in this way will be negligible.

Substitutes

Fluorspar is the only large scale commercial source of fluorine, and the ready availability of supplies in the United Kingdom makes it unlikely that competitive alternatives will emerge in this country in the near future. Calcined bauxite, topaz and unreclaimed cryolite bath, which consists mainly of aluminium together with appreciable quantities of sodium and aluminium fluorides, have been investigated as possible substitutes in the steel industry. During the Second World War small quantities of topaz were produced in the USA for use as a flux in steel manufacture, and as a glass opacifier.

Phosphate rock, which consists essentially of fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, may be considered to be a very large potential source of fluorine in view of the large quantities of fluorine compounds, largely silicon tetrafluoride (SiF_6), that are evolved during the manufacture of superphosphate. These compounds are removed from the waste gases by scrubbing in order to prevent air pollution. Only a small proportion of the fluosilicic acid so produced by the fertilizer industry in the United Kingdom is at present recovered as silico-fluorides and marketed. A considerable proportion of the phosphate rock imported is used to make phosphoric acid and in this process the fluorine compounds are not emitted in gaseous form. They are retained in the reaction solutions as very dilute fluosilicic acid, from which the recovery of fluorine compounds is hardly practicable. It is believed, however, that increasing cost of fluorspar will stimulate research into the wider use of these chemicals. The conversion of waste fluosilicic acid into synthetic acid-grade fluorspar or hydrofluoric acid has been investigated by the US Bureau of Mines. It is claimed that technically feasible processes have been developed but no commercial production based on these processes has been undertaken, as far as is known. Sodium fluosilicate, probably the most important metal fluosilicate made from fluosilicic acid, is used in water fluoridation and about 200 tonnes produced from phosphatic fertiliser manufacture are imported into the United Kingdom each year. In the USA the Aluminum Company of America (ALCOA) use fluosilicic acid in the manufacture of aluminium fluoride and synthetic cryolite; plants are reported to be in operation for this purpose also in Canada, France, Austria, India and, apparently, the USSR. The use of fluosilicic acid in the manufacture of aluminium fluoride is a recent development.

Industry

The Department of Trade and Industry, as the production department, maintains contact with the fluorspar industry through the British Fluorspar Producers Development and Research Association, Sheffield, and also with individual producing companies.

There are three major producers of fluorspar in the United Kingdom, as shown below, which are associated with either the steel or the chemical

industry. All operate mills, with either heavy-media separation or flotation plants, or both, to treat mined fluorspar. Approximately two-thirds of the output from these producers is utilised captively.

Derbyshire

Laporte Industries Limited
(General Chemicals Division)

Mines

Ladywash and Sallet Hole,
near Eyam

Durham

Weardale Lead Company
Limited (a)

Redburn, near Rookhope

British Steel Corporation

(Whiteheaps, near Hunstanworth
(Groverake, near Rookhope
(Blackdene, near St John's
Chapel

(a) Subsidiary of Imperial Chemical Industries Limited

The operations of Laporte Industries Limited expanded substantially during the 1960's, the company's share of the United Kingdom fluorspar market being 61 per cent in 1968 with sales of marketable products amounting to about 117,000 tonnes. Substantial tonnages of fluorspar are also exported by the company. The original Glebe mine was worked for lead between 1854 and 1884, was re-opened in 1937, and acquired by Laporte Industries in 1959. The Ladywash mine was also revived and underground contact established with Glebe. It was reported in June 1969 that production of fluorspar concentrates was at the rate of 129,500 tonnes per annum, of which 94,000 tonnes are of acid grade and 35,500 tonnes of metallurgical grade. Barytes and lead concentrates are produced as by-products. Most of the output from other producers in the surrounding area is processed at the Cavendish mill, the capacity of which is being raised from 70,000 tonnes to 120,000 tonnes per annum.

In County Durham an entirely new mine, the Redburn mine, has been worked since 1964 by the Weardale Lead Company. Production is around 20,000 tonnes of concentrate a year, comprising 12,000 tonnes acid-grade and 8,000 tonnes metallurgical-grade fluorspar. Annual production at the Blackdene mine, re-opened about 20 years ago by the United Steel Companies Limited, amounts to between 5,000 and 6,000 tonnes of metallurgical-grade fluorspar. It is reported that output will be increased to about 20,000 tonnes per annum when a new haulage level is completed. The Groverake and Whiteheaps mines produce about 10,000 to 12,000 tonnes per annum of metallurgical-grade fluorspar and considerably smaller quantities (3,000 to 4,000 tonnes) of acid-grade material from an enlarged mill. It is reported that production may possibly be increased to 50,000 tonnes per annum. The British Steel Corporation is to develop a mine at Allenheads, north-west of St John's Chapel. Of the remaining producers, two of the

largest are the Clay Cross (Land and Minerals) Limited, a subsidiary of Clay Cross Company Limited, who started operations at Milltown in Derbyshire shortly after the First World War and have been producing metallurgical-grade fluorspar for many years from Ashover in Derbyshire, and the Bleaklow Mining Company, who supply fluorspar to the Sheffield steel industry. The Clay Cross concern produces fluorspar briquettes for foundry use chiefly in the manufacture of SG (spheroidal graphite) iron; the output from the Ashover area is based on both mine and old dump operations. The Bleaklow Mining Company produce metallurgical-grade fluorspar and barytes by jigging at a plant near Calver, south-east of Eyam. Other important producers of fluorspar include A H Rockach Limited, whose output is derived from an opencast working on the Long Rake vein north of Youlgreave, and G E Bacon and Sons Limited, whose operations are situated on the same vein and also work dumps on the south side of Longstone Edge further to the north, near Hassop.

The total number of operators is not precisely known because production from some of those working dumps is not returned separately to the Department of Trade and Industry. In 1969 returns were received from 28 operators, of which 20 were in Derbyshire.

The prospective producer C E Giuliani (Derbyshire) Limited is a subsidiary of the Italian C E Giuliani group, which also owns Mineraria Silius SpA, a major world producer of fluorspar. A fluorspar flotation plant capable of treating 2,000 tonnes of ore per day is being installed at the Hopton works, about four miles south-west of Matlock, formerly owned by Magnesium Elektron Limited (a subsidiary of British Aluminium Limited). The plant is scheduled to come into operation in 1971, with an initial production capacity of about 68,000 tonnes of fluorspar, 25,000 tonnes of barytes and 6,000 tonnes of lead-zinc concentrates. The entire output of fluorspar, which will be solely of acid grade, is to be exported. The installation of the plant represents the most significant addition to United Kingdom fluorspar beneficiation capacity since the opening of Laporte Industries' Cavendish mill near Eyam in 1965. Feed for the Hopton mill will be derived from various tributaries and from extensive tailings at the old Millclose mine.

References

General

The markets for fluorite. D R Williamson. *Colo.Sch.Mines Miner.Ind.Bull.*, 1961, Vol.4, No.1. 12pp.

Fluorspar. C M Bartley, *Inf.Circ.No. I.C.127, Mines Brch Can.*, 1961. 55pp.

Investigation Reports on the Processing of Certain Materials in the Republic of South Africa and in South West Africa. Vol.5, Fluorspar. M K Oertel. 59pp. ([Pretoria]: Department of Planning, Natural Resources Development Council, 1966.)

Large scale plant trials of fluorspar substitutes. K R Narayan and S Visvanathan. *Tisco*, 1968, Vol.15, No.1, pp.18–22.

Forecasting future fluorspar needs. *Ind.Miner.,Lond.*, 1968, No.9, pp.9–13.

World fluorspar markets. *Ind.Miner.,Lond.*, 1968, No.9, pp.15–23, 25–26.

Fluorine recovery from phosphatic fertilizer manufacture. M English. *Chem.Process Engng*, 1967, Vol 48, No 12, pp 43-47.

Fluorspar metallurgy and flowsheets. F A Seeton. *Deco Trefoil*, 1970, Vol.34, No.1, pp.9–20.

Steelmakers face possible shortages of fluorspar. *Ind.Miner., Lond.*, 1970, No.33, pp.9–13.

World fluorspar industry. Pt.1. Europe and N America (excluding Mexico). Pt.2. Latin America, Africa and the Far East. *Ind.Miner.,Lond.*, 1970, No.33, pp.15–21, 23–27, 29; No.34, pp.21–28.

The adequacy of acid-grade fluorspar supplies questioned. *Ind.Miner.,Lond.*, 1970, No.34, pp.11–13, 15–19.

Utilization of waste fluosilicic acid (in two sections). 1 Laboratory investigations. 2 Cost evaluation. H E Blake, W S Thomas, K W Moser, J L Reuss and J Dolezal. *Rep.Invest.No 7502, US.Bur.Mines*, 1971. 60pp.

United Kingdom

The production of galena and associated minerals in the Northern Pennines: with comparative statistics for Great Britain. K C Dunham. *Trans. Instn Min. Metall.*, 1944, Vol.53, pp.181–214.

The structure and ore deposits of the Carboniferous Limestone of the Eyam district, Derbyshire. J Shirley and E L Horsfield. *Q.Jnl geol.Soc.Lond.*, 1945, Vol.100, Pts. 3 and 4, Nos. 399–400, pp.289–306.

Geology of the Northern Pennine Orefield. Vol.1. Tyne to Stainmore. K C Dunham. *Mem.geol.Surv.Engl.Wales*, 1948. 357pp.

Report of the Mineral Development Committee. *Cmd 7732, Minist.Fuel Pwr.* 106pp. (London: HM Stationery Office, 1949.) Fluorspar, pp.27–31.

Fluorspar. K C Dunham. *Mem.geol.Surv.spec.Rep.Miner.Resour. Gt.Br.*, 1952, Vol.4, 143pp.

Non-ferrous mining potentialities of the Northern Pennines. K C Dunham. pp.115–147, in *The Future of Non-Ferrous Mining in Great Britain and Ireland. A Symposium.* (London: The Institution of Mining and Metallurgy, 1959.)

The future of lead-zinc and fluorspar mining in Derbyshire. W W Varvill. pp.175–203, in *The Future of Non-Ferrous Mining in Great Britain and Ireland. A Symposium.* (London: The Institution of Mining and Metallurgy, 1959.)

County Development Plan Amendment. Written Analysis. J R Atkinson. 198pp. (County Council of Durham: 1964.) Fluorspar, pp.137–138.

Fluorspar production in Derbyshire and Yorkshire. W J Houston. *Quarry Mgrs' Jnl*, 1964, Vol.48, No.4, pp.149–154, 161.

Granite beneath Visean sediments with mineralization at Rookhope, northern Pennines. K C Dunham, A C Dunham, B L Hodge and G A L Johnson. *Q.Jnl geol.Soc.Lond.*, 1965, Vol.121, Pt.3, No.483, pp.383–414.

Le spath-fluor en Grande Bretagne. A Chermette. *Mines Métall.*, 1966, No.3605, pp.167–168, 170; No. 3606, pp.215–217; No.3607, pp.257–259; No.3608, pp.295–297; No. 3609, pp.335–337, 342; No.3610, pp.375–377; No.3611, pp.417–418. [In French.]

Some mineral deposits of the Carboniferous Limestone of Derbyshire. T D Ford. pp.53–75, *in* Geological Excursions in the Sheffield Region and the Peak District National Park. Edited by R Neves and C Downie. 163pp. (Sheffield: J W Northend Ltd., 1967.)

Peak District National Park Development Plan. First Review. Report and Analysis of Survey. J Foster. 124pp. ([Bakewell] : [Peak Park Planning Board] , 1966.) Vein minerals, p.16.

A summary of the mineral resources of the Crofter Counties of Scotland comprising Argyllshire, Caithness, Invernessshire Orkney and Shetland, Ross and Cromarty, and Sutherland. *Rep. No. 69/5 Inst.geol.Sci.*, 1969. 36pp. Fluorspar, p.29.

British Mining Fields. J E Metcalfe. 91pp. (London: The Institution of Mining and Metallurgy, 1969.) The Southern Pennines, pp.31-36; The Northern Pennines, pp.37–43.

The UK fluorspar industry and its basis. B L Hodge. *Ind.Miner.,Lond.*, 1970, No.31, pp.23, 25–29, 32–37.